II.B.10 Development of a Catalyst/Sorbent for Methane Reforming

Brent H. Shanks
Iowa State University
2207 Pearson Hall, Room 15
Ames, IA 50013
Phone: (515) 294-1895; E-mail: bshanks@iastate.edu

DOE Technology Development Manager:
Dan Cicero
Phone: (412) 386-4826
E-mail: Daniel.Cicero@netl.doe.gov

DOE Project Officer: Edgar Klunder
Phone: (412) 386-4678
E-mail: edgar.klunder@netl.doe.gov

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Objectives

- Optimize the production of hydrogen from methane where the methane must be reformed in the presence of steam to hydrogen and carbon dioxide.
- Conduct the steam reformation in the presence of both a catalyst for the reaction and a sorbent for the carbon dioxide thus achieving maximum efficiency.
- Prepare and test the new catalyst/calcium sorbent combination in a laboratory setting.

Introduction

The project involves the laboratory preparation and testing of a new material that combines a steam-methane reforming catalyst with a calcium-based sorbent for CO_2, one of the products of reforming. The new material will be in the form of small spherical pellets, which consist of a sorbent core surrounded by a porous shell with the catalyst. The pellets will be extensively characterized and tested to evaluate their performance and durability as a reforming catalyst and sorbent. The impact of different raw materials, preparation conditions, and usage conditions on catalyst/sorbent performance will be evaluated and used to optimize the preparation conditions to achieve a highly serviceable material.

Approach

The approach is to pelletize powdered limestone or dolomite to form the cores and then coat the cores with a mixture of powdered alumina and limestone followed by calcination to partially sinter the coating. The pellet shells are subsequently impregnated with a solution of nickel nitrate, heated to decompose the deposited nickel salt, and then treated with hydrogen to reduce nickel to its metallic state.

Accomplishments

The utility of the combined catalyst and sorbent has been demonstrated in laboratory experiments in which methane or carbon monoxide or both are reacted with steam to produce hydrogen in concentrations of 95% or more. Since the reforming reaction with steam takes place between 550 and 650ºC where carbon dioxide is also absorbed, the pellets can be regenerated by interrupting the flow of reactants and raising the temperature to 750ºC. Alternatively, when reforming is conducted under pressure, the pellets can be regenerated by reducing the pressure.

A new operating system has been assembled for this use which includes a larger fixed bed reactor capable of operation over a greater range of temperatures, pressures, and gas flow rates.

Conclusions and Future Directions

The development of a promising material for use in steam reforming methane was advanced by showing that the principal components of the combined catalyst and sorbent can be improved through changes in their formulation and treatment. The apparent absorption capacity and stability of the CaO sorbent was shown to be highly dependent on the nature and particle size of its precursor. The physical strength and surface area of the catalyst supporting shell material were shown to depend on the nature and amount of higher surface area alumina incorporated in the mixture of alumina particles which comprised 90 to 97% of the shell forming material. The catalytic activity of the prepared catalyst, as indicated by the conversion of methane, was directly proportional to the nickel content of the catalyst, and it was much greater for steam reforming at 750°C than at 600°C.

In the future further improvements in both the sorbent material and shell material/catalyst support will be made. Several problems have been identified and will be addressed. They arise from the high temperature instability of the materials which results in a decline in surface area of both the calcium-based sorbent and the alumina catalyst support as the pellets are heated to the high temperatures required for fabrication and utilization.

Core-in-shell pellets will be prepared using the best formulations which have been found for the individual components. The pellets will be evaluated by reacting steam with methane and/or carbon monoxide at different temperatures and pressures with and without hydrogen sulfide present. The physical strength of the pellets will be measured, and limited life-cycle testing of the most promising pellets will be conducted.

FY 2006 Publications/Presentations

1. J. A. Satrio, B. H. Shanks, and T. D. Wheelock, "A combined Catalyst and Sorbent for Enhancing Hydrogen Production from Coal or Biomass", submitted to *Energy & Fuels*, March, 2006.

References

1. J. A. Satrio, B. H. Shanks, and T. D. Wheelock, "Development of a Novel Combined Catalyst and Sorbent for Hydrocarbon Reforming", *Ind. Eng. Chem. Res.*, **44**, 3901-3911 (2005).

2. J. A. Satrio, B. H. Shanks, and T. D. Wheelock, "A Combined Catalyst and Sorbent for Enhancing Hydrogen Production form Coal", presented at the Clearwater Coal Conference, Clearwater, Florida, April 17-21, 2005.

3. B. H. Shanks and T. D. Wheelock, "Development of a Catalyst/Sorbent for Methane Reforming", poster presentation at the DOE University Coal Research Contractors Review Meeting, Pittsburgh, PA, June, 2005.